

Gruneisen parameter and binding energy for lead using model potential approach

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Gruneisen parameters and binding energy for lead have been calculated using a two parameter model potential. The results compare well with the available experimental results. The possible factors influencing the discrepancy between the calculated and observed properties have been discussed.

1. INTRODUCTION

The phonon dispersion relations of sodium and potassium have been calculated by Kushwaha & Rajput (1970) using a two parameter model potential and the results have been found satisfactorily agreeing with the available experimental data. The calculations of the Gruneisen's parameters, specific heat, binding energies were also carried out on these metals by Kushwaha and Rajput (1975).

Such calculations do not stringently test the validity of model potential because the response of conduction electrons to the vibrating ions in alkali metals, through which pseudopotential enters the calculations, accounts for a relatively small proportion of the effective interaction between the ions. In the case of f.c.c. lead, the screening of conduction electrons is much greater as compared with alkali metals. We have therefore thought it worthwhile to study the similar properties of lead and the present paper deals with the calculation of Gruneisen parameter and its binding energies. Earlier Prasad & Srivastava (1973) has carried out such calculations using Krasko & Gurskii (1970) model.

2. NUMERICAL COMPUTATION

The total crystal energy E is composed of the electrostatic energy E^{es} and the total conduction electron energy E^e . In the electronic ground state the total conduction electron energy E^e is given by

$$E^e = \text{electron gas part} + \text{band structure part} \\ = E^{eg} + E^{bs} \quad \dots (1)$$

The electron gas energy per electron is $(3/5) \epsilon_F + \epsilon_x + \epsilon_c + v_{core}^0$ where, ϵ_F is the usual Fermi energy and ϵ_x , ϵ_c are the exchange and correlation energies per electron respectively. The last term v_{core}^0 is the $q = 0$ matrix element of the ion-core part. The details of the electrostatic energy contribution have been given by Kellermann (1940).

The band structure energy per ion is

$$E^0_s = \sum S^*(q) F(q) S(q) \quad \dots (2)$$

where $F(q)$ is the energy wave number characteristic being given by

$$F(q) = -\frac{\Omega_0 q^2}{8\pi z e^2} \frac{|V_q^0|^2}{[1-f(q)]} \frac{\epsilon(q)-1}{\epsilon(q)} \quad \dots (3)$$

V_q^0 is the bare ion form factor, Ω_0 is the atomic volume and $E(q)$ is the Hartree dielectric function. The function $f(q)$ is the correlation function which takes into account the exchange and correlation interactions. The expression for $f(q)$ as given by Hubbard (1958) is,

$$f(q) = \frac{q^2}{2(q^2 + \xi k_F^2)} \quad \dots (4)$$

where ξ is a function of electron density which is obtained by Geldard *et al* (1966) from the compressibility equation

$$\xi = \frac{2}{[1 + 0.153/(\pi a_0 k_F)]} \quad \dots (5)$$

a_0 being Bohr's radius and k_F the Fermi surface wave vector. The bare-ion form factor in terms of two parameters α and β is written as

$$V_q^0 = \frac{1}{\Omega_0} \frac{4\pi Z e^2}{q^2 + \alpha^2} \left[-\frac{\alpha^2}{q^2} + \frac{\alpha\beta}{q^2 + \alpha^2} \right] \quad \dots (6)$$

For $q = 0$, the ion core part is given by

$$V_{core}^0 = \frac{4\pi Z e^2}{\Omega_0 \alpha^3} \quad \dots (7)$$

The determinantal equation for calculating angular frequencies is written in the usual way as

$$\det |D_{ij}(q) - m\omega_{qp}^2 \delta_{ij}| = 0$$

Here q is the phonon wave vector, p is the polarization branch and m is the mass of the ion, $D_{ij}(q)$ are the elements of the dynamical matrix. i, j are the cartesian components (x, y, z). $D_{ij}(q)$ is expressible as the sum of three terms

$$D_{ij}(q) = D_{ij}^C(q) + D_{ij}^R(q) + D_{ij}^E(q) \quad \dots (8)$$

$D_{ij}^C(q)$ originates from bare coulomb interaction between the ions and $D_{ij}^R(q)$ is the contribution from overlap potential between the ions. We neglect $D_{ij}^R(q)$ assuming that the overlapping between the cores is negligible. $D_{ij}^E(q)$ stems from the ion-electron-ion interaction. Expressions for $D_{ij}^E(q)$ for f.c.c. lattice are taken from Kellermann's work (1940).

(i) *Gruneisen's Parameters*

The Gruneisen parameters are defined by

$$\gamma_{qp} = -(\partial \ln \omega_{qp} / \partial \ln \Omega_0)$$

The mean value of γ_{qp} is given by

$$\gamma_M = \frac{\sum_{qp} \gamma_{qp} E(\hbar \omega_{qp} / k_B T)}{\sum_{qp} E(\hbar \omega_{qp} / k_B T)},$$

where $E(x) = \frac{x^2 e^x}{(e^x - 1)^2}$ and k_B is Boltzman constant.

(ii) *Binding Energy*

The energy of a solid contains terms resulting from the electron-ion-electron and ion-ion interactions in addition to the usual kinetic, exchange and correlation energies

The total energy per electron of the system can be written as

$$\begin{aligned} E = & \frac{2.21}{r_0^2} - \frac{0.916}{r_0} + (-0.115 + 0.031 \log r_s) - \frac{1.792 Z^{2/3}}{r_0} \\ & + \frac{\alpha}{(4/3)\pi r_0^3} - \sum_{q \neq 0} A(q) \frac{1}{r_0^4} f(t) \quad \dots \quad (9) \end{aligned}$$

where
$$A(q) = \frac{9}{32\pi^2(12\pi^2)^{1/3}} |V_q^0|^2$$

$$f(t) = 1 + \frac{1-t^2}{2t} \log \left| \frac{1+t}{1-t} \right| \quad \text{with } t = \frac{q}{2k_F}$$

and

r_0 = atomic radius

The first three terms of eq. (9) are kinetic, exchange and correlation energies of the interacting electron gas. For the latter, we have chosen Nozières-Pines (1966) form because none of the existing formulae differ more than 10% for this range of r_0 . The fourth term is the second order contribution to the ion-ion interaction. The fifth term is the zeroth Fourier coefficient (first order) contribution of both the interactions. The last term is the second order contribution of the electron-ion interaction.

A consistent value of α is now obtained by minimising the total energy of the system using the equilibrium or zero pressure condition

$$P = -\frac{1}{4\pi r_0} \frac{dE}{dr_0} = 0$$

$$\text{This gives } \frac{3\alpha}{4\pi r_0^2} = -\frac{2}{3} \frac{2}{r_0^2} + \frac{1}{3} \frac{(0.916 + 1.792Z^{2/3})}{r_0}$$

$$+ 0.1 + \frac{1}{3} \sum_{q \neq 0} A(q) \frac{1}{r_0^4} \left[3 - \frac{5-3t^2}{2t} \log \left| \frac{1+t}{1-t} \right| \right]$$

Substituting for α in eq. (9), the binding energy of the system is (2)

$$E_b = \frac{0.737}{r_0^2} - \frac{2}{3} \frac{(0.916 + 1.792Z^{2/3})}{r_0} + (-0.150 + 0.031 \log r_0) + \frac{3}{16\pi^2(12\pi^2)^{1/3}} + \frac{1}{r_0^4} \left(\sum_{q \neq 0} \frac{|V_q^0|^2}{2t} \log \left| \frac{1+t}{1-t} \right| \right) \quad \dots (10)$$

The compressibility χ is defined as the second derivative of the total energy of the system with respect to r_0 at the minimum i.e.

$$\frac{1}{\chi} = \frac{1}{12\pi r_0} \left. \frac{d^2 E}{dr_0^2} \right|_{E_{min}}$$

The compressibility χ in terms of free electric compressibility χ_0 is expressed as

$$\frac{\chi_0}{\chi} = \frac{1}{22.1} \left[0.093r_0^2 + 2(0.916 + 1.792Z^{2/3}) - 4.42 + \frac{1}{r_0^2} \frac{9}{32\pi^2(12\pi^2)^{1/3}} \sum_q \frac{2|V_q^0|^2}{1-t^2} \left(1 - \frac{5(1-t^2)}{2t} \log \left| \frac{1+t}{1-t} \right| \right) \right] \quad \dots (11)$$

The value of χ_0 is $1.7r_0^5$

The following data is used in our calculations

$$\Omega_\infty = 20.34, \quad \alpha = 4, \quad \beta = 46, \quad \epsilon = 0.458, \quad k_F = 0.835 \text{ and } r_s = 3.648$$

3. RESULTS AND DISCUSSION

(i) Gruneisen Parameters :

In figure 1 we have plotted the one phonon Gruneisen parameter curves for longitudinal and transverse modes in three principal symmetry directions. It is observed that in [100] direction the calculated γ_{qp} decreases with increasing q for longitudinal mode and it increases with increasing q for transverse mode.

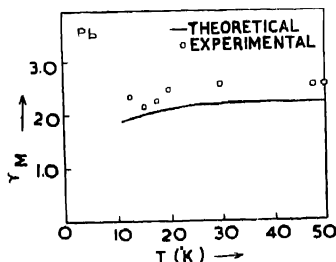


Fig. 1 Theoretical γ_{qp} is shown (curves) along [100], [110] and [111] symmetry direction

Similarly in [111] direction γ_{qp} is found to increase for longitudinal branch with increasing q while it is found to decrease for transverse branch. In figure 2 we have plotted the temperature variation of γ_M along with the experimental points of Channing *et al* (1965). It is observed that γ_M increases consistently with

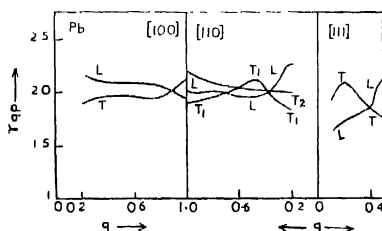


Fig. 2 Theoretical mean Gruneisen Constant is plotted (curves) as a function of temperature. Experimental points (open circle) have also been plotted

increasing T upto 30°K and thereafter it becomes constant. The rapid changes in γ_{qp} curves may be attributed to the observed Kohn anomalies in the dispersion curves.

(ii) Compressibility and Binding Energy

Ashcroft (1966) has given the experimental values for binding energy and compressibility ratio for lead. Ashcroft & Langreth (1967) computed these values

with good agreement We have given our calculated values along with the theoretical values of Ashcroft in table 1

Table 1. Binding Energy and compressibility of lead

	Binding energy ($-E_b$) ryd/electron	Compressibility ratio χ/χ_0
Experimental	1.79	3.5
Theoretical (Authors)	1.83	3.56
Theoretical (Ashcroft and Langreth)	1.55	3.2

The table shows that our calculated values compare well with the experimental values as well as theoretical values of Ashcroft & Langreth (1967).

The present model potential does not reproduce all the measured properties because it is assumed that lead has got spherical Fermi surface. In fact the Fermi surface of lead is much distorted. Moreover, the effect of spin-orbit coefficient is pronounced in lead as pointed out by Anderson & Gold (1965). The results can be further improved by modifying the wave function in light of above facts and also by including higher order pseudopotential terms in the dynamical matrix as pointed out by Harrison (1966) and Brovman *et al* (1968).

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